Near-Infrared Absorbing Organoruthenium Complexes: Crystal Violet Analogues

Iuan-Yuan Wu, Jiann T. Lin,* and Yuh S. Wen

Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan, Republic of China

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Replacement of "NR_2" substituents in crystal violet (or ethyl violet) by "$CpRu(PPh_3)_2(C{\equiv}C)$" results in formation of stable derivatives of triaryl carbocations, $\{[CpRu(PPh_3)_2(C{\equiv}CC_6H_4\text{-}4)][Et_2NC_6H_4\text{-}4]_2\}C^+$ (**3**$^+$) and $\{[CpRu(PPh_3)_2(C{\equiv}CC_6H_4\text{-}4)]_2[Me_2NC_6H_4\text{-}4]\}C^+$ (**5**$^+$), and $\{[CpRu(PPh_3)_2(C{\equiv}CC_6H_4\text{-}4)]_3\}C^+$ (**7**$^+$). They were isolated as BF_4 salts. The stable carbocation $\{[CpRu(PPh_3)_2(C{\equiv}C\text{-th}((E)\text{-}CH{=}CH)\text{-th})][Et_2NC_6H_4\text{-}4]_2\}C^+$ (**6**$^+$) (th = 2,5-substituted thiophene), has also been synthesized. These complexes exhibit intense electronic absorption in the near-infrared region. Incorporation of thiophene rings was shown to enhance both λ_{max} and f values.

Introduction

There currently is much interest in the development of new infrared absorbing dyes because these materials are useful in several fields: laser optical recording systems, laser printing systems, laser thermal writing displays, infrared photography, and mechanical or biological applications.[1] Research related to nonlinear optical materials has shown that conjugating systems with strong electron donors and acceptors, and/or with extended conjugation, typically show more favorable bathochromatic shifts in the charge-transfer absorption.[2] Conceptually, these strategies can be applied to the construction of near-infrared absorbing dyes. Indeed, by choosing a powerful electron acceptor, thioflavylium, and incorporating thiophene rings into the conjugation chain, Chen and Marder were successful in synthesizing several organic near-infrared absorbing dyes.[3] Recently, we,[4] and Humphrey and co-workers[5] have also demonstrated that the "$CpRu(PPh_3)_2$" moiety in the ruthenium σ-acetylides of the push−pull type is a very effective electron donor which can considerably lower the energy of the charge-transfer band in the visible region. Thus, if a potent electron acceptor such as the cationic seven-membered tropylium ring[6] is linked to $CpRu(PPh_3)_2$, a low-lying charge transfer from the electron donor to the tropylium group is attainable if there exists an efficient conjugation path between the two. Toward this end, we set out to synthesize a new class of near-infrared absorbers based on coupling the aforementioned ruthenium σ-acetylides with a triphenylcarbenium moiety as the acceptor. These NIR absorbers can be expected to exhibit high ϵ's. In this report, we describe the synthesis and characterization of several novel organoruthenium NIR absorbers.

Table 1. Crystal Data for Compound 1·CH_2Cl_2

chem formula	$C_{64}H_{54}Cl_2OP_2Ru$
fw	1073.05
cryst size, mm	0.16 × 0.44 × 0.69
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	11.301(7)
b, Å	15.255(3)
c, Å	15.982(5)
α, deg	102.11(2)
β, deg	96.94(4)
γ, deg	99.16(3)
V, Å^3	2626(2)
Z	2
T, °C	+20
F(000)	1108
λ(Mo Kα), Å	0.7107
ρ_{calc}, g cm^{-3}	1.357
μ, cm^{-1}	4.957
transm coeff	1.00−0.95
$2\theta_{max}$, deg	50
h, k, l range	−13 to 13, 0 to 18, −18 to 18
tot no. of reflns	9740
no. of unique reflns	9229
no. of obsd reflns ($I > 2.0\sigma(I)$)	7696
refined params	631
R^a	0.038
$R_w{}^b$	0.046
GOF(F^2)^c	2.04

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o) + kF_o^2]$ where $k = 0.0001$. ^{c} $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ where n = no. of obsd reflns and p = no. of variables.

Experimental Section

General Procedures. All reactions and manipulations were carried out under N_2 with the use of standard inert-atmosphere and Schlenk techniques. Solvents were dried by standard procedures. All column chromatography was per-

* Corresponding author. Fax: Int. code +(2)27831237. E-mail: jtlin@chem.sinica.edu.tw.

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formed with the use of silica gel (230−400 mesh ASTM, Merck) as the stationary phase in a column 35 cm in length and 2.5 cm in diameter. Compounds $Cp(PPh_3)_2Ru(C{\equiv}CC_6H_4Br\text{-}p)$,[7] $Cp(PPh_3)_2Ru(C{\equiv}C\text{-th-}(E)\text{-}CH{=}CH\text{-th-}Br)$ (th = 2,5-substituted thiophene),[8] $Cp(PPh_3)_2RuCl$,[9] $PdCl_2(PPh_3)_2$,[10] 4,4′-diethynylbenzophenone,[11] and (4-bromophenylethynyl)trimethylsilane[12] were prepared by published procedures. Infrared measurements were measured on a Perkin-Elmer 880 spectrometer. The NMR spectra were recorded on Bruker AMX400 (^1H, ^{13}C, ^{31}P) and AC300 (^1H, ^{31}P) spectrometers. Electronic absorption spectra were obtained on a Perkin-Elmer Lambda 9 spectrometer. Mass spectra (EI) were recorded on a VG70-250S mass spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer.

$Cp(PPh_3)_2Ru(C{\equiv}CC_6H_4C(OMe)Ph_2)$ (1). To a flask containing a mixture of 4-bromobenzophenone (1.31 g, 5.0 mmol), $PdCl_2(PPh_3)_2$ (70 mg, 0.10 mmol), and CuI (10 mg, 0.050 mmol) was added Et_2NH (50 mL) and trimethylsilylacetylene (0.85 mL, 6.0 mmol) under a nitrogen atmosphere. The mixture was stirred at room temperature for 5 h. The solvent was removed under vacuum, and the residue was extracted with CH_2Cl_2/H_2O. The organic layer was collected, dried over $MgSO_4$, filtered through Al_2O_3, and pumped dry. The redidue was recrystallized from CH_2Cl_2/hexane to afford pale brown crystalline 4-(trimethylsilylethynyl)benzophenone in 93% yield (1.30 g). ^1H NMR (300 MHz, C_6D_6, 25 °C, TMS): $\delta = 0.25$ (s, 9 H, CH_3), 7.44−7.74 (m, 9 H, Ph and C_6H_4). MS (EI): *m/e* 278 (M^+), 263 ($M^+ - CH_3$). To a Et_2O solution (100 mL) of 4-(trimethylsilylethynyl)benzophenone (1.39 g, 5.0 mmol) prechilled to −30 °C was slowly added a solution of phenyllithium (3.33 mL, 6.0 mmol, 1.8 M in cyclohexanes/ether). The solution was slowly warmed to room temperature and stirred for 4 h. One milliliter of H_2O was added, and the solution was stirred for 30 min. Additional H_2O (>200 mL) was added, and the organic layer was collected, dried over $MgSO_4$, filtered through Al_2O_3, and pumped dry. The residue was chromatographed using CH_2Cl_2/hexane (2:1) as eluent to afford (4-ethynylphenyl)diphenylmethanol (**1a**) as a pale yellow oil in 81% yield (1.24 g). This substance was spectroscopically identical with bona fide **1a**.[13]

To a mixture of $Cp(PPh_3)_2RuCl$ (0.36 g, 0.50 mmol) and **1a** (0.16 g, 0.56 mmol) was added 50 mL of MeOH. The resulting mixture was refluxed for 3 h. The solution was cooled to 0 °C, and Na (18 mg, 0.80 mmol) was added slowly. The solution was filtered, and the yellow solid was washed with MeOH (3 × 10 mL) and hexane (3 × 5 mL). The crude product was recrystallized from CH_2Cl_2/hexane to afford **1** as a yellow powder in 77% yield (0.38 g). Anal. Calcd for $C_{63}H_{52}OP_2Ru$: C 76.58, H 5.30. Found: C 76.31, H 5.21. ^1H NMR (300 MHz, C_6D_6, 25 °C, TMS): $\delta = 3.05$ (s, 3 H, CH_3), 4.44 (s, 5 H, Cp), 7.51 (d, $J = 8.4$ Hz, 2 H, C_6H_4), 7.56 (d, 2 H, C_6H_4), 6.88−7.10 and 7.62−7.74 (m, 40 H, PPh_3 and Ph); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 52.0$ (OCH_3), 85.2 (Cp), 87.1 ($C(C_6H_4)Ph_2$), 114.3 ($Ru{-}C{\equiv}C_\beta$), 116.9 (t, $J_{C-P} = 24.0$ Hz, $Ru{-}C_\alpha{\equiv}C$), 126.6 (Ph), 127.2 (t, $J = 4.5$ Hz, C_{meta} of PPh_3), 127.6 (Ph), 128.4 (C_{para} of PPh_3), 128.6 (Ph), 128.7 (C_6H_4), 129.3 (C_6H_4), 129.7 (C_6H_4), 133.8 (t, $J_{C-P} = 5.0$ Hz, C_{ortho} of PPh_3), 137.4 (C_6H_4), 138.9 (t, $J_{C-P} = 20.7$ Hz, C_{ipso} of PPh_3), 144.8 (Ph). ^{31}P NMR (120 MHz, C_6D_6, 25 °C, 85% H_3PO_4): $\delta = 51.5$. IR (KBr, cm^{-1}): 1089 (s, C−O), 2073 (vs, C≡C).

$[Cp(PPh_3)_2Ru(C{\equiv}CC_6H_4C(C_6H_4X\text{-}p)Ph)][BF_4]$ (1b, X = H; 2b, X = OMe). Excess $H^+BF_4^-$ (54% Et_2O solution) was slowly added to a THF solution of **1** prechilled to 0 °C. The resulting mixture was stirred for 5 min, and Et_3N was added. The complex **1b** formed was characterized by electronic spectra only. Attempted isolation of **1b** resulted in recovery of **1**. Complex **2b** was synthesized in a manner similar to that employed for **1b**, except that (4-methoxy)phenyllithium (prepared in situ from 4-bromoanisole and *t*-BuLi) was utilized instead of phenyllithium. Complex **2b** was also characterized by electronic spectra only. The two key precursors, (4-ethynylphenyl)(4′-methoxyphenyl)phenylmethanol (**2a**) and $Cp(PPh_3)_2Ru(C{\equiv}CC_6H_4C(OMe)(C_6H_4OMe\text{-}p)Ph)$ (**2**), were isolated and characterized. **2a**: Anal. Calcd for $C_{22}H_{18}O_2$: C 84.05, H 5.77. Found: C 84.04, H 5.81. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.70$ (br, 1 H, O*H*), 3.04 (s, 1 H, ≡C*H*), 3.78 (s, 3 H, OCH_3), 6.81 (d, $J = 8.3$ Hz, 2 H, C_6H_4−O), 7.13 (d, 2 H, C_6H_4−O), 7.21−7.29 (m, 7 H, Ph and C_6H_4), 7.41 (d, $J = 8.4$ Hz, 2 H, C_6H_4). **2**: Anal. Calcd for $C_{64}H_{54}O_2P_2Ru$: C 75.50, H 5.35. Found: C 75.36, H 5.24. ^1H NMR (300 MHz, C_6D_6, 25 °C, TMS): $\delta = 3.13$ (s, 3 H, OCH_3), 3.32 (s, 3 H, OCH_3), 4.49 (s, 5 H, Cp), 6.67 (d, $J = 8.8$ Hz, 2 H, C_6H_4−O), 7.55 (d, 2 H, C_6H_4−O), 7.61 (d, $J = 8.8$ Hz, 2 H, C_6H_4), 7.64 (d, 2 H, C_6H_4), 6.90−7.23, 7.71−7.77 (m, 35 H, PPh_3 and Ph). ^{31}P NMR (120 MHz, C_6D_6, 25 °C, 85% H_3PO_4): $\delta = 51.6$. IR (KBr, cm^{-1}): 1089, 1178 (s, C−O), 2073 (vs, C≡C).

$[Cp(PPh_3)_2Ru(C{\equiv}CC_6H_4C(C_6H_4NEt_2\text{-}p)_2)][BF_4]$ (3). A solution of *t*-BuLi (0.71 mL, 1.21 mmol, 1.7 M in pentane) was added to a solution of $Cp(PPh_3)_2Ru(C{\equiv}CC_6H_4Br\text{-}p)$ in 25 mL of Et_2O prechilled to −78 °C. The solution was then stirred at −30 °C for 15 min. After the solution was further warmed to room temperature and stirred for 30 min, 4,4′-bis(diethylamino)benzophenone (0.35 g, 1.1 mmol) in 20 mL of THF was slowly added and stirred for 16 h. After addition of 1 mL of H_2O, the solvent was removed in vacuo and the residue extracted with CH_2Cl_2. The extract was filtered through Celite and concentrated. Yellow powders formed upon addition of hexane. The powders were collected and dried to provide $Cp(PPh_3)_2Ru(C{\equiv}CC_6H_4)C(OH)(C_6H_4NEt_2\text{-}p)_2$ in 70% yield. ^1H NMR (300 MHz, CD_3CN, 25 °C, TMS): $\delta = 1.10$ (t, $J = 7.0$ Hz, 12 H, CH_3), 3.31 (q, 8 H, CH_2), 4.28 (s, 5 H, Cp), 6.62 (d, $J = 8.9$ Hz, 4 H, NC_6H_4), 6.97 (d, NC_6H_4), 7.10−7.46 (m, 34 H, PPh_3 and C_6H_4). ^{31}P NMR (120 MHz, CD_3CN, 25 °C, 85% H_3PO_4): $\delta = 48.6$. This crude compound was dissolved in 25 mL of THF and cooled to 0 °C. A solution of HBF_4 (0.30 mL, 54% in Et_2O) was added, and the resulting mixture was stirred for 5 min. Et_3N (1 mL) was added, and the resulting green solution was pumped dry. The residue was first washed with Et_2O/hexane (1:1) until the washing was clear, then washed rapidly with H_2O and dried. Recrystallization of the crude product from CH_2Cl_2/hexane afforded green powdery **3** in 68% yield (0.81 g). Anal. Calcd for $C_{70}H_{67}BF_4N_2P_2Ru$: C 70.88, H 5.69, N 2.36. Found: C 70.67, H 5.71, N 2.50. Mp = 176 °C. ^1H NMR (300 MHz, CD_3CN, 25 °C, TMS): $\delta = 1.26$ (t, $J = 7.1$ Hz, 12 H, CH_3), 3.60 (q, 8 H, CH_2), 4.41 (s, 5 H, Cp), 6.94 (d, $J = 9.4$ Hz, 4 H, NC_6H_4), 7.14−7.43 (m, 38 H, PPh_3 and C_6H_4). ^{13}C NMR (100 MHz, CD_3CN, 25 °C, TMS): $\delta = 11.9$ (CH_3), 45.4 (CH_2), 86.1 (Cp), 110.0 ($Ru{-}C{\equiv}C_\beta$), 112.8 (NC_6H_4), 121.9 (C_6H_4), 126.6 (NC_6H_4), 127.5 (C_{meta} of PPh_3), 128.9 (C_{para} of PPh_3), 130.4 (C_6H_4), 133.8 (C_{ortho} of PPh_3), 136.2 (C_6H_4), 137.5 (C_6H_4), 138.5 (t, $J_{C-P} = 21.1$ Hz, C_{ipso} of PPh_3), 140.4 (NC_6H_4), 146.0 (t, $J_{C-P} = 24.6$ Hz, $Ru\text{-}C_\alpha{\equiv}C$), 154.6 ($NC_6H_4$), 176.7 ($CPh_3$). ^{31}P NMR (120 MHz, CD_3CN, 25 °C, 85% H_3PO_4): $\delta = 48.5$. IR (KBr, cm^{-1}): 1073 (s, BF_4), 2017 (s, C≡C). Vis/NIR (CH_2Cl_2, λ_{max} (nm), ϵ (10^4 M^{-1} cm^{-1}): 609 nm, $\epsilon = 8.25$, $f = 0.62$; 725 nm, $\epsilon = 3.79$, $f = 0.49$.

$[Cp(PPh_3)_2Ru(C{\equiv}CC_6H_4)]_2C(O)$ (4). To a flask containing a mixture of 4,4′-dibromobenzophenone (5.0 g, 14.7 mmol), $PdCl_2(PPh_3)_2$ (0.42 mg, 0.60 mmol), and CuI (60 mg, 0.30

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mmol) was added THF (100 mL), $^{i}Pr_2NH$ (20 mL), and trimethylsilylacetylene (4.6 mL, 32.5 mmol) under a nitrogen atmosphere. The mixture was stirred at room temperature for 40 h. The solvent was removed under vacuum, and the residue was extracted with CH_2Cl_2/H_2O. The organic layer was collected, dried over $MgSO_4$, filtered through Al_2O_3, and pumped dry. The residue was recrystallized from CH_2Cl_2/hexane at −30 °C to afford pale brown crystalline 4,4′-bis(trimethylsilylethynyl)benzophenone (**4a**) in 96% yield (5.29 g). ^{1}H NMR (300 MHz, C_6D_6, 25 °C, TMS): δ = 0.25 (s, 18 H, C*H*$_3$), 7.53 (d, J = 8.6 Hz, 4 H, C$_6$*H*$_4$), 7.69 (d, 4 H, C$_6$*H*$_4$). To a mixture of **4a** (1.0 g, 2.67 mmol) and KOH (0.30 g, 5.36 mmol) was added 50 mL of MeOH, and the solution was stirred at room temperature for 3 h. The solution was then extracted with Et_2O. The Et_2O solution was pumped dry, and the residue was chromatographed using EtOAc/hexane (1:50 to 1:5) as eluent to afford 4,4′-diethynylbenzophenone (**4b**) in 68% yield (0.42 g). This substance was spectroscopically identical with bona fide **4b**.[14]

To a mixture of $Cp(PPh_3)_2RuCl$ (1.45 g, 2.0 mmol), **4b** (0.23 g, 1.0 mmol), and $NH_4^+PF_6^-$ (0.33 g, 2.1 mmol) were added 50 mL of MeOH and 40 mL of CH_2Cl_2. The resulting mixture was refluxed for 3 h. The solution was cooled to room temperature, and 3 mL of Et_3N was added. After the solvent was removed, the residue was chromatographed using EtOAc/hexane (1:5) as eluent to afford **4** as a yellow powder was in 65% yield (1.05 g). Anal. Calcd for $C_{99}H_{78}OP_4Ru_2$: C 73.87, H 4.88. Found: C 73.50, H 4.49. ^{1}H NMR (300 MHz, CD_3CN, 25 °C, TMS): δ = 4.39 (s, 10 H, Cp), 7.16−7.54 (m, 60 H, PPh$_3$), 7.21 (d, J = 8.3 Hz, 4 H, C$_6$*H*$_4$), 7.61 (d, 4 H, C$_6$*H*$_4$). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 85.4 (Cp), 116.0 (Ru−C≡*C*$_\beta$), 127.2 (t, J_{C-P} = 24.6 Hz, Ru-*C*$_\alpha$≡C), 127.3 (C$_{meta}$ of PPh$_3$), 128.5 (C$_{para}$ of PPh$_3$), 129.9 (*C*$_6$H$_4$), 130.1 (*C*$_6$H$_4$), 132.6 (*C*$_6$H$_4$), 133.8 (t, J_{C-P} = 5.1 Hz, C$_{ortho}$ of PPh$_3$), 134.5 (*C*$_6$H$_4$), 138.7 (t, J_{C-P} = 20.9 Hz, C$_{ipso}$ of PPh$_3$), 195.7 (*C*O). ^{31}P NMR (120 MHz, CD_3CN, 25 °C, 85% H_3PO_4): δ = 48.7. IR (KBr, cm^{-1}): 1640 (m, CO), 2062 (vs, C≡C).

[{Cp(PPh$_3$)$_2$Ru(C≡CC$_6$H$_4$)}$_2$C(C$_6$H$_4$NMe$_2$)][BF$_4$] (5). A solution of *t*-BuLi (0.78 mL, 1.33 mmol, 1.7 M in pentane) was added to a solution of 4-bromo-*N*,*N*-dimethylaniline (0.12 g, 0.60 mmol) in 20 mL of THF prechilled to −78 °C. The solution was then stirred at −30 °C for 15 min. The solution was further warmed to room temperature and stirred for 30 min. This solution was slowly added to a solution of [Cp(PPh$_3$)$_2$Ru-(C≡CC$_6$H$_4$)]$_2$CO (**4**) (0.80 g, 0.50 mmol) in 20 mL of THF, and the mixture was stirred at room temperature for 16 h. After addition of 1 mL of H_2O, the solvent was removed in vacuo and the residue extracted with CH_2Cl_2. The extract was filtered through Celite and concentrated. A yellow powder formed upon addition of hexane. The powder was collected and dried to provide [Cp(PPh$_3$)$_2$Ru(C≡CC$_6$H$_4$)]$_2$C(OH)(C$_6$H$_4$NMe$_2$) in 65% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.63 (s, 6 H, C*H*$_3$), 4.56 (s, 10 H, Cp), 6.54 (d, J = 8.9 Hz, 2 H, NC$_6$*H*$_4$), 7.54 (d, 2 H, NC$_6$*H*$_4$), 7.61 (d, J = 8.5 Hz, 4 H, C$_6$*H*$_4$), 7.68 (d, 4 H, C$_6$*H*$_4$), 7.02−7.83 (m, 60 H, PPh$_3$). ^{31}P NMR (120 MHz, $CDCl_3$, 25 °C, 85% H_3PO_4): δ = 50.3. This crude compound was dissolved in 25 mL of THF and cooled to 0 °C. A solution of HBF_4 (0.20 mL, 54% in Et_2O) was added, and the resulting mixture was stirred for 5 min. Et_3N (1 mL) was added, and the resulting green solution was pumped dry. The residue was first washed with Et_2O/hexane (1:1) until the washing was clear, then washed rapidly with H_2O, and dried. Recrystallization of the crude product from CH_2Cl_2/hexane afforded green powdery **5** in 74% yield (0.67 g). Anal. Calcd for $C_{107}H_{88}BF_4NP_4Ru_2$: C 71.37, H 4.93, N 0.78. Found: C 70.98, H 4.82, N 0.59. Mp = 185 °C. ^{1}H NMR (300 MHz, CD_3CN, 25 °C, TMS): δ = 3.29 (s, 6 H, C*H*$_3$), 4.44 (s, 10 H, Cp), 6.99 (d, J = 9.3 Hz, 2 H, NC$_6$*H*$_4$), 7.12−7.44 (m, 68 H, PPh$_3$ and C$_6$*H*$_4$), 7.51 (d, 2 H, NC$_6$*H*$_4$). ^{13}C NMR (100 MHz, CD_3CN, HMBC & HMQC, 25 °C, TMS): δ = 40.8 (*C*H$_3$), 86.6 (Cp), 113.3 (NC*C*H), 127.5 (C$_{meta}$ of PPh$_3$), 128.2 (NCCHCH*C*), 128.3 (Ru−C≡*C*$_\beta$), 128.9 (C$_{para}$ of PPh$_3$), 131.2 (C≡CC*C*H), 133.6 (C$_{ortho}$ of PPh$_3$), 134.1 (C≡C*C*), 136.8 (C≡CCCH*C*H), 138.0 (t, J_{C-P} = 21.4 Hz, C$_{ipso}$ of PPh$_3$), 139.3 (C≡CCCHCH*C*), 140.6 (NCCH*C*H), 156.5 (CH$_3$N*C*), 158.7 (t, J_{C-P} = 24.6 Hz, Ru-*C*$_\alpha$≡C), 176.7 (*C*(C$_6$H$_4$)$_3$). ^{31}P NMR (120 MHz, CD_3CN, 25 °C, 85% H_3PO_4): δ = 48.4. IR (KBr, cm^{-1}): 1085 (m, BF_4), 1995 (vs, C≡C), 2035 (sh, C≡C). Vis/NIR (CH_2Cl_2, λ_{max} (nm), ϵ (10^4 M^{-1} cm^{-1})): 740 nm, ϵ = 6.78, f = 1.08; 855 nm, ϵ = 7.74, f = 0.84.

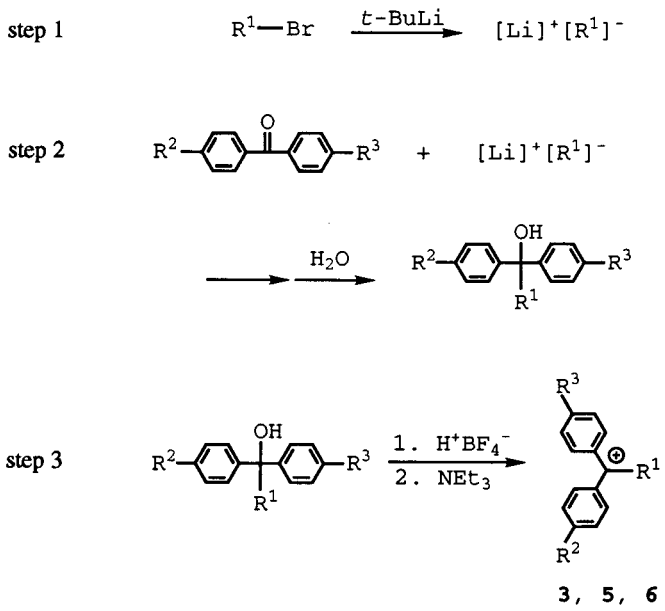
[Cp(PPh$_3$)$_2$Ru(C≡C-th-(*E*)-CH=CH-th-C(C$_6$H$_4$NEt$_2$)$_2$]-[BF$_4$] (6). Complex **6** was synthesized by the same procedure as employed for **3** except that Cp(PPh$_3$)$_2$Ru(C≡C-th-(*E*)-CH=CH-th-Br) (th = 2,5-substituted thiophene)[8] was used instead of Cp(PPh$_3$)$_2$Ru(C≡CC$_6$H$_4$Br-*p*). Dark blue powdery **6** was isolated in 70% yield. Anal. Calcd for $C_{74}H_{69}BF_4N_2P_2S_2Ru$: C 68.35, H 5.35, N 2.15. Found: C 68.20, H 5.22, N 2.07. T_{decomp} = 156 °C. ^{1}H NMR (300 MHz, CD_3CN, 25 °C, TMS): δ = 1.25 (t, ^3J = 6.8 Hz, 12 H, C*H*$_3$), 3.59 (q, 8 H, C*H*$_2$), 4.36 (s, 5 H, Cp), 6.54 (d, J = 3.8 Hz, 1 H, SCC*H*), 6.94 (d, J = 9.3 Hz, 4 H, C$_6$*H*$_4$), 6.97 (d, 1 H, J = 16.5 Hz, 1 H, =C*H*), 7.09−7.50 (m, 38 H, PPh$_3$, =C*H*, SCC*H*, and C$_6$*H*$_4$). ^{13}C NMR (100 MHz, CD_3CN, 25 °C, TMS): δ = 12.0 (*C*H$_3$), 45.3 (*C*H$_2$), 85.8 (Cp), 110.0 (Ru−C≡*C*$_\beta$), 110.6 (N*C*$_6$H$_4$), 124.8 (S*C*=), 125.5 (N*C*$_6$H$_4$), 127.3 (*C*$_6$H$_4$), 127.4 (*C*$_6$H$_4$), 127.5 (t, J_{C-P} = 4.6 Hz, C$_{meta}$ of PPh$_3$), 128.3 (*C*$_6$H$_4$), 128.8 (*C*$_6$H$_4$), 128.9 (C$_{para}$ of PPh$_3$), 133.5 (t, J_{C-P} = 4.9 Hz, C$_{ortho}$ of PPh$_3$), 133.6 (N*C*$_6$H$_4$), 134.0 (S*C*=), 138.6 (t, J_{C-P} = 21.0 Hz, C$_{ipso}$ of PPh$_3$), 139.3 (t, J_{C-P} = 24.0 Hz, Ru-*C*$_\alpha$≡C), 146.8 (S*C*= or *C*(C$_6$H$_4$)$_2$th), 153.1 (*C*(C$_6$H$_4$)$_2$th or S*C*=), 154.1 (N*C*$_6$H$_4$). ^{31}P NMR (120 MHz, CD_3CN, 25 °C, 85% H_3PO_4): δ = 48.0. IR (KBr, cm^{-1}): 1085 (m, BF_4), 2009 (vs, C≡C). Vis/NIR (CH_2Cl_2, λ_{max} (nm), ϵ (10^4 M^{-1} cm^{-1})): 897 nm, ϵ = 6.74, f = 0.88.

[{Cp(PPh$_3$)$_2$Ru(C≡CC$_6$H$_4$)}$_3$C][BF$_4$] (7). A solution of *n*-BuLi (2.1 mL, 3.36 mmol, 1.6 M in hexane) was added to a solution of (4-bromophenylethynyl)trimethylsilane (0.69 mg, 2.74 mmol) in 50 mL of Et_2O prechilled to −78 °C. The solution was then stirred at −30 °C for 15 min. The solution was warmed to room temperature, stirred for 1 h, and cooled to −30 °C. A THF solution (20 mL) of **4a** (0.83 g, 2.19 mmol) prechilled to −30 °C was added slowly, and the resulting mixture was stirred for 15 min. The solution was warmed to 0 °C and stirred for 2 h. After addition of 1 mL of H_2O the solution was pumped dry. The residue was chromatographed using CH_2Cl_2/hexane (1:5 to 2:1) as eluent to afford tris(4-(trimethylsilylethynyl)phenyl)methanol (**7a**) as a colorless powder in 77% yield (0.92 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.22 (s, 27 H, C*H*$_3$), 2.72 (s, 1 H, O*H*), 7.13 (d, J = 8.4 Hz, 6 H, C$_6$*H*$_4$), 7.38 (d, 6 H, C$_6$*H*$_4$). To a mixture of **7a** (0.92 g, 1.68 mmol) and KOH (0.28 g, 5.0 mmol) was added 50 mL of MeOH, and the solution was stirred at room temperature for 3 h. The solution was then extracted with Et_2O. The Et_2O solution was pumped dry, and the residue was chromatographed using EtOAc/hexane (1:50 to 1:5) as eluent to afford tris(4-ethynylphenyl)methanol (**7b**) as a colorless powder in 84% yield (0.47 g). Anal. Calcd for $C_{34}H_{40}Si_3O$: C 74.39, H 7.34. Found: C 74.03, H 7.28. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.73 (s, 1 H, O*H*), 3.06 (s, 3 H, ≡CH), 7.19 (d, J = 8.2 Hz, 6 H, C$_6$*H*$_4$), 7.43 (d, 6 H, C$_6$*H*$_4$). IR (KBr, cm^{-1}): 1018 (m, C−O), 2107 (w, C≡C); 3554(m, O−H).

To a mixture of $Cp(PPh_3)_2RuCl$ (1.20 g, 1.65 mmol), **7b** (166 mg, 0.50 mmol), and $Tl^+PF_6^-$ (0.55 g, 1.58 mmol) were added 30 mL of MeOH and 20 mL of THF. The resulting mixture was heated at 80 °C for 3.5 h. The solution was cooled to room temperature and a solution NaOMe, prepared in situ from Na (60 mg) and MeOH (10 mL), was added. After filtration the yellow solid was chromatographed using EtOAc/hexane (2:3 to 1:2) as eluent. The yellow powdery [Cp(PPh$_3$)$_2$Ru(C≡CC$_6$H$_4$)]$_3$C(OMe) (**7c**) was isolated in 30% yield (0.36 g). Anal. Calcd for $C_{148}H_{118}OP_6Ru_3$: C 74.02, H 4.95. Found: C 73.70, H 5.01. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.08 (s,

(14) Royles, B. J. L.; Smith, D. M. *J. Chem. Soc., Perkin Trans. 1* **1984**, *4*, 355.

Scheme 1



compd	R^1	R^2	R^3
3	[Ru]-C≡C-C_6H_4	NEt_2	NEt_2
5	$C_6H_4NMe_2$	[Ru]-C≡C	[Ru]-C≡C
6	[Ru]-C≡C-th-CH=CH-th	NEt_2	NEt_2

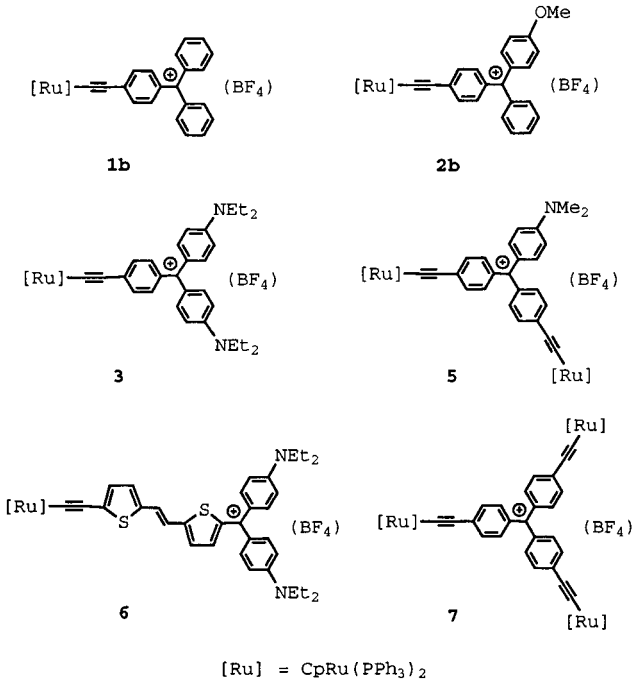
[Ru] = $CpRu(PPh_3)_2$; th = 2,5-substituted thiophene

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 1·CH_2Cl_2

Distances			
Ru−C1	2.241(3)	C9−C10	1.384(5)
Ru−C2	2.235(4)	C10−C11	1.386(4)
Ru−C3	2.223(3)	C11−C12	1.391(4)
Ru−C4	2.258(3)	C12−C13	1.380(5)
Ru−C5	2.242(3)	C13−C8	1.390(5)
Ru−C6	2.022(3)	C11−C14	1.543(4)
Ru−P1	2.287(1)	C14−C21	1.530(5)
Ru−P2	2.293(2)	C14−C31	1.533(5)
C6−C7	1.210(4)	C14−O	1.446(4)
C7−C8	1.439(4)	C15−O	1.416(5)
C8−C9	1.404(5)		
Angles			
P1−Ru−P2	102.14(5)	C11−C14−C31	105.7(3)
P1−Ru−C6	86.89(9)	C21−C14−C31	112.5(3)
P2−Ru−C6	87.3(1)	C11−C14−O	111.0(2)
Ru−C6−C7	178.0(3)	C21−C14−O	108.8(3)
C6−C7−C8	175.0(4)	C31−C14−O	104.9(2)
C11−C14−C21	113.6(3)		

3 H, OCH_3), 4.29 (s, 15 H, Cp), 7.04−7.09, 7.15−7.21, 7.45−7.49 (m, 102 H, PPh_3 and C_6H_4). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 52.0$ (OCH_3), 85.2 (Cp), 87.2 ($C(C_6H_4)_3$), 114.5 (Ru−C≡C_β), 115.0 (t, $J_{C-P} = 24.8$ Hz, Ru−C_α≡C), 127.2 (t, $J_{C-P} = 4.4$ Hz, C_{meta} of PPh_3), 128.6 (C_{para} of PPh_3), 128.6 (C_6H_4), 129.6 (C_6H_4), 129.6 (C_6H_4), 133.9 (t, $J_{C-P} = 4.9$ Hz, C_{ortho} of PPh_3), 139.0 (t, $J_{C-P} = 20.8$ Hz, C_{ipso} of PPh_3), 139.2 (C_6H_4); ^{31}P NMR (120 MHz, $CDCl_3$, 25 °C, 85% H_3PO_4): $\delta = 51.0$. IR (KBr, cm^{-1}): 1089 (m, s, C−O), 2072 (vs, C≡C). A solution of $H^+BF_4^-$ (0.2 mL, 54% Et_2O solution) was slowly added to a THF (5 mL) solution of **7c** (80 mg, 0.033 mmol) prechilled to 0 °C. The resulting mixture was stirred for 5 min, and 0.5 mL of Et_3N was added. The volume of the solution was reduced to

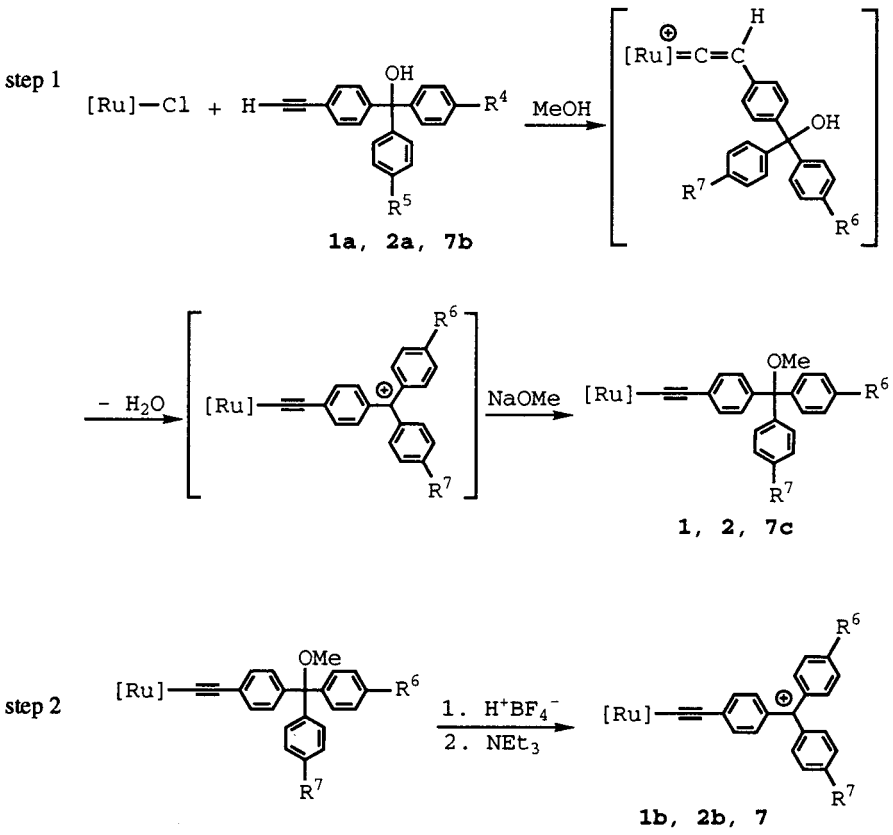
Chart 1



[Ru] = $CpRu(PPh_3)_2$

2 mL, and 25 mL of Et_2O was added. The solution was filtered, and the solid was washed with H_2O and Et_2O. The crude product was recrystallized from CH_2Cl_2/hexane to afford green powdery **7**·$2CH_2Cl_2$ in 80% yield (82 mg). Anal. Calcd for $C_{150}H_{121}BCl_4F_4P_6Ru_3$: C 68.21, H 4.62. Found: C 68.17, H 4.83. $T_{decomp} = 197$ °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): 4.47

Scheme 2



compd	R^4	R^5	R^6	R^7
1a	H	H		
2a	H	OMe		
7b	HC≡C	HC≡C		
1			H	H
2			H	OMe
7c			[Ru]-C≡C	[Ru]-C≡C
1b			H	H
2b			H	OMe
7			[Ru]-C≡C	[Ru]-C≡C

[Ru] = $CpRu(PPh_3)_2$

(s, 15 H, Cp), 5.27 (s, 4 H, CH_2Cl_2), 7.10−7.16, 7.25−7.28, 7.36−7.44 (m, 102 H, Ph and C_6H_4). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 87.0$ (Cp), 127.6 ($J_{C-P} = 4.7$ Hz, C_{meta} of PPh_3), 128.4 (Ru−C≡C_β), 128.9 (C_{para} of PPh_3), 131.6 (C_6H_4), 133.7 (t, $J_{C-P} = 5.1$ Hz, C_{ortho} of PPh_3), 135.4 (C_6H_4), 136.9 (C_6H_4), 137.6 (t, $J_{C-P} = 21.6$ Hz, C_{ipso} of PPh_3), 139.9 (C_6H_4), 166.2 (t, $J_{C-P} = 23.5$ Hz, Ru-C_α≡C), 174.2 ($C(C_6H_4)_3$). ^{31}P NMR (120 MHz, $CDCl_3$, 25 °C, 85% H_3PO_4): $\delta = 50.8$. IR (KBr, cm^{-1}): 1090 (m, BF_4), 1986 (vs, C≡C). Vis/NIR (CH_2Cl_2, λ_{max} (nm), ϵ (10^4 M^{-1} cm^{-1}): 974 nm, $\epsilon = 11.5$, $f = 1.34$.

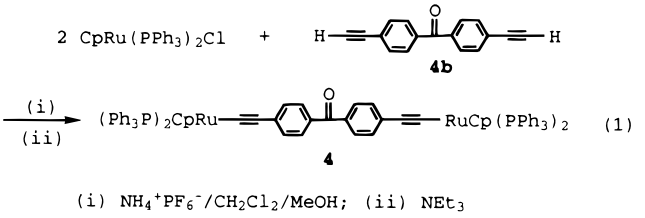
Crystallographic Studies. Crystals of **1**·CH_2Cl_2 were grown by slow diffusion of hexane into a concentrated solution of **1** in CH_2Cl_2. Crystals were mounted on a glass fiber covered with epoxy. Data were collected at 294 K on an Enraf-Nonius CAD4 diffractometer by using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) with the $\theta-2\theta$ scan mode. Unit cells were determined by centering 25 reflections in the suitable 2θ range. Other relevant experimental details are listed in Table 1. The structure was solved by direct methods using NRCVAX[15] and refined by full-matrix least-squares (based on F^2) using SHELXL-93. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were were placed in idealized positions with $d_{C-H} = 0.95$ Å. The selected interatomic distances and bond angles are given in Table 2. All other crystal data for **2**·CH_2Cl_2 are given in the Supporting Information.

Results and Discussion

Syntheses of Ruthenium Trityl Complexes. Ruthenium trityl complexes synthesized in this study are

(15) Gabe, E. J.; LePage, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

depicted in Chart 1. Complexes **3**, **5**, and **6** were synthesized via three major sequential steps (Scheme 1): (1) the conversion of aryl bromides to aryl anions;[16] (2) the reaction of appropriate diaryl ketones with aryllithium compounds to form triaryl carbinols;[17] (3) the protonation of the carbinols by HBF_4[18] followed by treatment with NEt_3. The new diaryl ketone, **4**, was prepared from the reaction of $CpRu(PPh_3)_2Cl$ with 4,4′-diethynylbenzophenone according to the well-known procedure[19] (eq 1). The triaryl carbinols formed in the



second step were characterized spectroscopically (Experimental Section), and the crude compounds were used for further reactions. Upon acid treatment of the carbinols in the step 3, the formation of triaryl carbocations is believed to occur with concurrent protonation of the β-carbon atoms of ruthenium σ-acetylides and the dialkylamino substituents on phenyl rings. Et_3N was found to be effective to deprotonate these intermediates without detriment to the carbocations (vide infra). We were not able to synthesize **7** from the reaction of $Cp(PPh_3)_2Ru(C{\equiv}CC_6H_4Li\text{-}p)$ with **4**, a pathway similar to that described in Scheme 1, possibly due to the steric crowding of the two reactants. Complexes **7**, **1b**, and **2b** were prepared according to the sequential steps in Scheme 2. Triphenyl carbinols were synthesized before the incorporation of the ruthenium σ-acetylide moiety, and analytically pure ruthenium σ-acetylides in which the triphenyl carbinol moiety is converted to methyltriphenylmethylether could be isolated (step 1). The protonation of methyltriphenylmethylether with HBF_4 followed by treatment with NEt_3 then affords the desired triaryl carbocations (step 2).[20] The kinetic stability of these new trityl complexes varies with the nature of the acceptor. For instance, the complexes **1b** and **2b** readily react with NaOMe to reform the starting materials and can only be characterized by electronic absorption spectra (**1b**, $\lambda_{max} = 766$ nm; **2b**, $\lambda_{max} = 819$ nm in CH_2Cl_2), We were able to trap **1b** by MeOH to form **1**, the structure of which was confirmed by single-crystal X-ray analysis (vide infra).

It is well-known that dyes of the crystal violet[21] type are fairly stable under ambient conditions. Therefore,

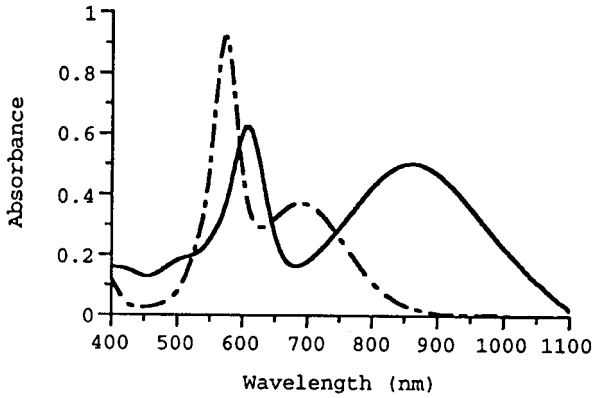
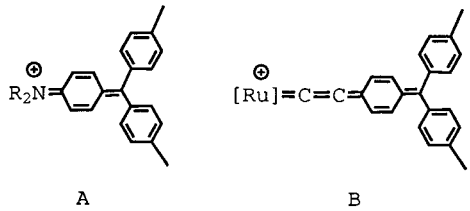


Figure 1. Electronic spectra (1.25×10^{-5} M in CH_2Cl_2) of complexes **3** (dashed) and **6** (solid).

Chart 2



the introduction of dialkylamino substituents on the phenyl rings of **1b** should enhance the stability of the carbocation. Indeed, we have prepared and characterized two unsymmetrical crystal violet analogues, **3** and **5** (Chart 1). We have also synthesized complex **6**, which incorporates a thiophene ring in the conjugation chain. The resonance interaction of the dialkylamino moiety with the carbocation certainly (vide infra) enhances the stability of **3**, **5**, and **6 versus 1b** and **2b**. Complex **7**, in which all three "NMe_2" substituents in the crystal violet are replaced by "$Cp(PPh_3)_2Ru(C{\equiv}C)$", has also been synthesized. The stability of **7** may be attributed to the efficient dissipation of the positive charge throughout the multimetal centers, similar to 1,1,5,5,-tetraferrocenylpenta-2,3,4-trienylium[22] and $[Cp^*(dppe)Ru{=}C{=}C{=}CHC{\equiv}CRu(dppe)Cp^*]^+$.[23] Complexes **3** and **5**−**7** are stable in common solvents, including MeOH and H_2O, under ambient conditions in air.

Spectroscopic Studies. The spectroscopic properties of the new organoruthenium trityl complexes are consistent with their formulations. The prominent feature of the carbocations is the rather downfield shift (153.1−176.7 ppm) in the ^{13}NMR spectra for the carbon atom bearing the positive charge.[18,24] The presence of the ruthenium σ-acetylide moiety in the complexes is supported by a characteristic downfield shift of $\delta(C_\alpha)$ (139.3−166.2) in the ^{13}NMR spectra and the existence of a $\nu(C{\equiv}C)$ stretching (1986−2035 cm^{-1}) in the infrared spectra.[19] In these complexes, the importance of the canonical resonance form A (Chart 2) as a contributor to the ground electronic state is supported by the NMR spectroscopic data: (1) the methylene protons of NEt_2 in **3** ($\delta = 3.60$ ppm) and **6** ($\delta = 3.59$ ppm) or the methyl

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Table 3. Absorption Constants for Organometallic and Organic NIR Absorber

compound	λ_{max} (nm)	ϵ (10^{-4} M^{-1} cm^{-1})	f
5	855	7.74	0.84
6	897	6.74	0.88
7	974	11.5	1.34
(*E*)-1-ferrocenyl-2-(4-thioflavyliumyl)ethylene perchlorate[a]	852	1.3	0.25
[{Fe(η^5-C_5Me_5)(η^2-dppe)}$_2$(μ-C≡C−C≡C)][PF_6][b]	1302	1.2	
[Cp(PPh_3)$_2$Os(μ-CN)Ru(NH_3)$_5$][CF_3SO_3]$_3$[c]	851	0.34	0.11
[CpFe(η^5-C_5H_4)CH═CH(η^7-C_7H_6)][PF_6][d]	816	0.55	
[CpFe(η^5-C_5H_4)Z(η^7-C_7H_6)][PF_6],[d] Z = thiophene-1,5-diyl	845	1.12	0.18
Fc(CH═CH)$_n$Fc (Fc =ferrocenyl, n = 1−6)[e]	1647−2036	0.13−0.21	
[{(η^5-C_5H_5)$_2$Fe$_2$(CO)$_2$(μ-CO)}$_2$(μ-C-(CH═CH)$_3$-CH═C)][BF_4][f]	730	24.3	1.37
1,1,5,5-tetraferrocenylpenta-2,3,4-trien-1-ylium tetrafluoroborate[g]	917	1.78	0.36
D−(CH═CH)$_3$−A (*D* = julolidinyl, A = thioflavylium)[h]	882	9.3	1.55
[4,4′-bis(*N*,*N*-di-*p*-methoxyphenylamino)tolane]$^{+i}$	1751	2.23	0.35

[a−f] References 27a−f. [g] Reference 22. [h] Reference 3. [i] Reference 27g.

protons (δ = 3.29 ppm) of NMe_2 in **5** exhibit chemical shifts at much lower field than those of their alcohol precursors in which no resonance from the amino group is possible (NEt_2, 3.31 ppm; NMe_2, 2.90 ppm in CD_3-CN); (2) the chemical shifts of the methylene protons of NEt_2 in **3** and **6** are similar to those of ethyl violet (δ = 3.56 ppm in CD_3CN) and at lower field than those of the methylene protons of *N*,*N*-diethylaniline (δ = 3.35 ppm in CD_3CN). However, it is apparent that canonical resonance form B cannot be neglected in light of the following observations: (1) the chemical shifts of the α-carbon atoms in the "ruthenium σ-acetylide" moiety appear at significantly lower field than those of typical ruthenium σ-acetylides;[4a,5] (2) the C≡C stretching frequencies of **3** and **5**−**7** occur in the low energy region among ruthenium σ-acetylides.[19]

Unsymmetrical dyes of crystal violet (or malachite green) analogues normally exhibit two types of absorption bands, the *x* and *y* bands.[25] These two bands are observed for **3**, **5**, and **6**. Contribution of the ruthenium moiety to the low-lying electronic absorption is most evident from the considerable bathochromic shift of the electronic absorption spectra of **1b** (λ_{max} = 766 nm in CH_2Cl_2), **3** (λ_{max} = 725 nm in CH_2Cl_2), **5** (λ_{max} = 855 nm in CH_2Cl_2), and **6** (λ_{max} = 897 nm in CH_2Cl_2) compared with those of ethyl violet (λ_{max} = 587 nm in CH_2Cl_2) and several azulene analogues (λ_{max} < 630 nm in CH_3CN) of the triphenyl methyl cation.[26] Incorporation of the thiophene ring is expected to lower the energy of the charge-transfer transitions.[4b] Indeed, complex **6** exhibits a substantially bathochromic shift for λ_{max} compared to **3** (Figure 1). The complex **7**, which is symmetrical in structure, exhibits the longest λ_{max} (974 nm) and the highest f (1.34) among the complexes in this study. Moreover, **7**, as well as **5** and **6**, exhibits the highest absorption intensity among organometallic complexes which absorb at λ_{max} = 800 nm (Table 3).

Lewis reported that increasing the number of NR_2 substituents decreased the λ_{max}.[25a] Our results are in accordance with this trend: **7** > **5** > **3**, in order of decreasing λ_{max}. Therefore, the dialkylamino moiety helps to stabilize the trityl cations at the expense of λ_{max}.

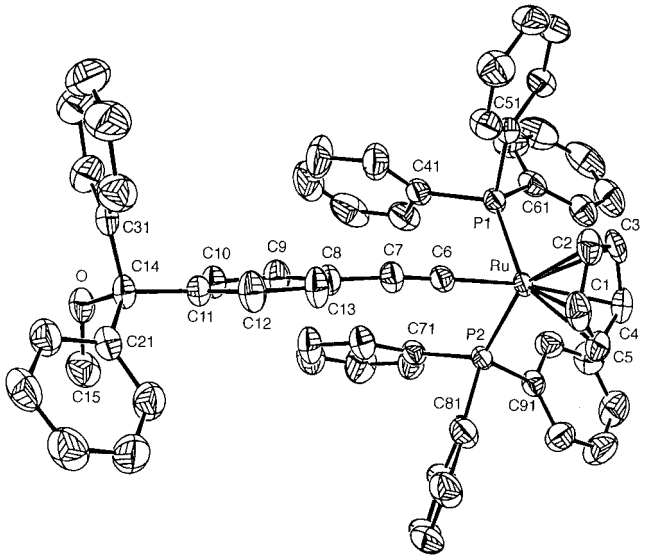

Figure 2. ORTEP drawing of complex **1**. Thermal ellipsoids are drawn with 50% probability boundaries.

Molecular Structures of Cp(PPh_3)$_2$Ru(C≡CC_6H_4C(OMe)Ph_2) (1·CH_2Cl_2). An ORTEP drawing of **1** is shown in Figure 2. Humphrey suggested that the presence of a strong acceptor acetylide ligand might lengthen the Ru−P distance.[5b] Ru−P distances (2.287(1), 2.293(2) Å) for **1** are substantially longer than those in Ru(C≡CPh)(PPh_3)$_2$(η^5-C_5H_5) (2.228(3), 2.229(3) Å)[28] despite the absence of a strong acceptor. The Ru−C6 distance (2.022(3) Å) is somewhat long among related ruthenium(II) σ-acetylide complexes,[19c] although no apparent steric interaction is found to exist inter- or intramolecularly. C6−C7 (1.210(4) Å) and C7−C8 (1.439(4) Å) distances as well as Ru−C6−C7 (178.0(3)°) and C6−C7−C8 (175.0(4)°) angles all fall within the range observed for similar complexes.[19c]

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Conclusion

We have synthesized several organoruthenium analogues of crystal violet. We found that incorporation of dialkylamino and "$Cp(PPh_3)_2Ru(C{\equiv}C)$" substituents on the phenyl rings of the triphenylcarbenium ion resulted in the formation of stable organoruthenium near-infrared absorbers. In addition, incorporation of thiophene rings increases the λ_{max} as well as the oscillating strength of the complexes. Further research in this area to fine-tune λ_{max} and enhance the f values is currently under investigation. Preliminary results indicate that substitution of the ferrocenylvinyl moiety for the ruthenium σ-acetylide moiety also leads to stable near-infrared dyes.[29]

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Supporting Information Available: Tables of atomic coordinates and thermal parameters, all bond distances and angles, and experimental data for X-ray diffraction studies of **1**·CH_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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